



The  
Patent  
Office

PCT/GB 99/03076

16 SEPTEMBER 1999

09/787358

INVESTOR IN PEOPLE

GB99/3076

The Patent Office  
Concept House  
Cardiff Road  
Newport  
South Wales  
NP10 8QQ

REC'D 23 NOV 1999

WIPO PCT

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules

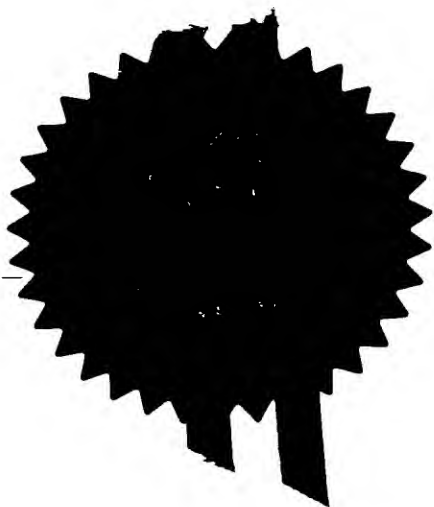
**PRIORITY  
DOCUMENT**

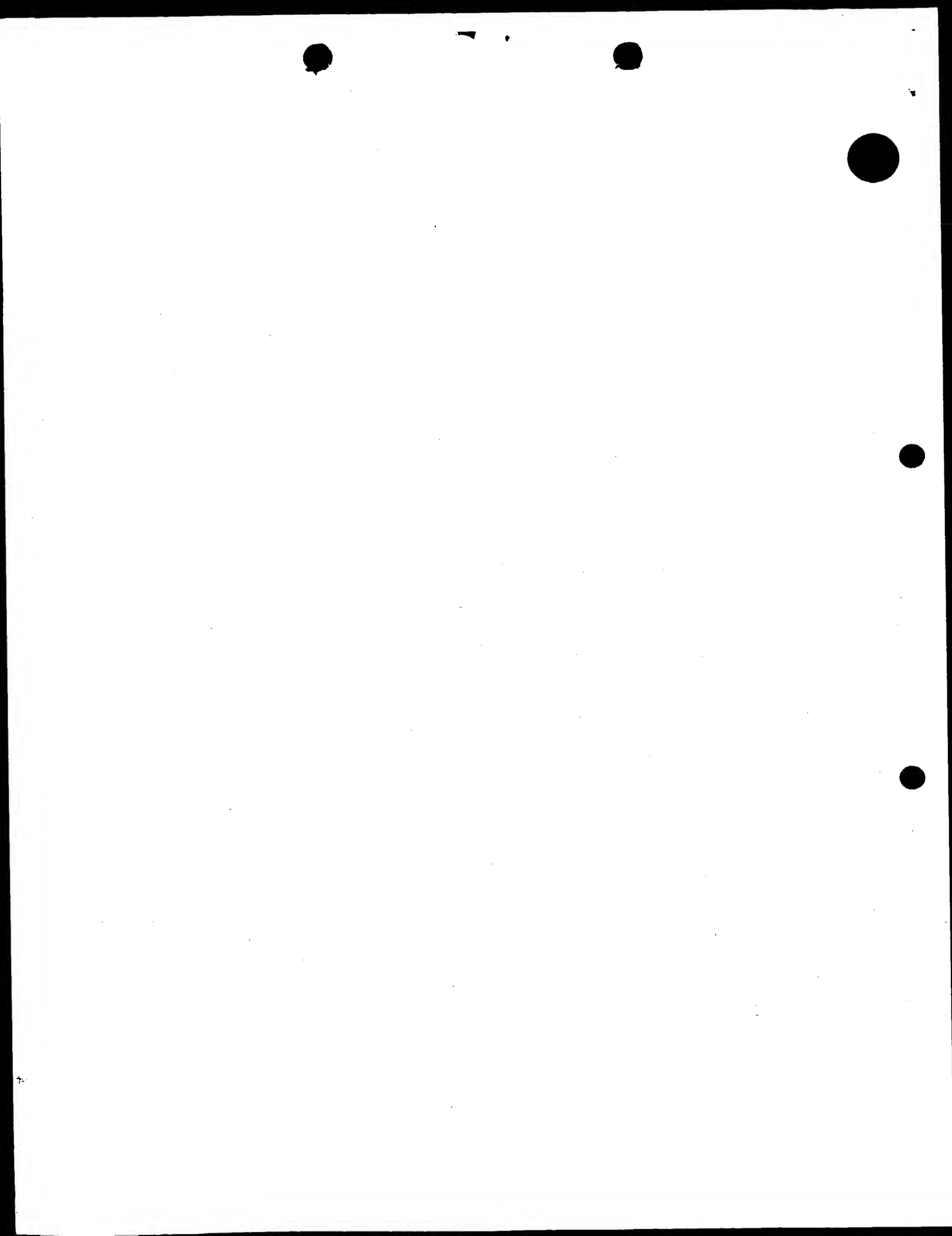
SUBMITTED OR TRANSMITTED IN  
COMPLIANCE WITH RULE 17.1(a) OR (b)

Signed

Dated

23 NOV 1999





THE PATENT OFFICE  
16 SEP 1998

**Request for the grant of a patent**

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road  
Newport  
Gwent NP9 1RH

1. Your reference

SNR06119GB

2. Patent application number

(The Patent Office will fill in this part)

16 SEP 1998

9820210.4

3. Full name, address and postcode of the or of each applicant (underline all surnames)

VG Elemental Limited  
c/o Thermo Elemental Limited  
Pickfords Wharf  
Click Street  
London  
SE1 9DG

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

Great Britain

7/14367001

4. Title of the invention

Means for Removing Unwanted  
Ions from an Ion Transport  
System and Mass Spectrometer

5. Name of your agent (if you have one)

GILL JENNINGS & EVERY

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Broadgate House  
7 Eldon Street  
London  
EC2M 7LH

Patents ADP number (if you know it)

745002

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number  
(if you know it)

Date of filing  
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing  
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

- a) any applicant named in part 3 is not an inventor
  - b) there is an inventor who is not named as an applicant, or
  - c) any named applicant is a corporate body.
- See note (d))

# Patents Form 1/77

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form

Description

10

Claim(s)

Abstract

Drawing(s)

1

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11. For the Applicant  
Gill Jennings & Every

I/We request the grant of a patent on the basis of this application.

Signature

Date

12. Name and daytime telephone number of person to contact in the United Kingdom

RACKHAM, Stephen Neil  
0171 377 1377

## Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

## Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

MEANS FOR REMOVING UNWANTED IONS FROM AN ION TRANSPORT  
SYSTEM AND MASS SPECTROMETER

5       The present invention relates to inductively coupled  
plasma mass spectrometry (ICPMS). However, the concepts  
can be applied to any type of mass spectrometer which  
generates unwanted artefact ions as well as ions of  
analytical significance, such artefact ions having  
10       properties that allow them to be selectively removed from  
the ion beam by causing them to interact with a reagent gas  
whilst the ions of analytical significance are  
substantially retained in the beam.

      The general principles of ICPMS are well known. It is  
a method of elemental analysis providing information about  
15       the elemental composition of a sample, with little or no  
information about its molecular structure. Typically, the  
sample is a liquid, which is nebulised and then passed  
through an electrically-maintained plasma, in which the  
temperature is high enough to cause atomization and  
20       ionisation of the sample. Typically temperatures greater  
than 5000K are used. The ions produced are introduced, via  
one or more stages of pressure reduction, into a mass  
analyzer. The mass analyzer is most commonly a quadrupole,  
although magnetic sector analyzers are also used and, more  
25       recently, time-of-flight devices.

      A problem common to all of these, although most  
troublesome in low-resolution devices such as quadrupoles,  
is the presence in the mass spectrum of unwanted artefact  
ions that impair the detection of some elements. The  
30       identity and proportion of artefact ions depends upon the  
chemical composition of both the plasma support gas and  
that of the original sample. There are many such artefact  
ions. Typical are argon-containing molecular ions that are  
encountered in argon-based ICPMS, which is the most wide-  
35       spread technique. Argon oxide ( $\text{ArO}^+$ ) and argon dimer ( $\text{Ar}_2^+$ )  
are prominent, and interfere with the detection of iron  
( $^{56}\text{Fe}$ ) and selenium ( $^{80}\text{Se}$ ) respectively.

A collision cell may be used to remove unwanted artefact ions from an elemental mass spectrum. The use of a collision cell is described in EP 0 813 228 A1 and WO 97/25737.

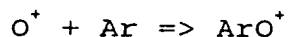
5        A collision cell is a substantially gas-tight enclosure through which ions are transmitted. It is positioned between the ion source and the main spectrometer. A target gas is admitted into the collision cell, with the objective of promoting collisions between  
10        ions and the neutral gas molecules or atoms. The ions are confined in the cell by means of multipole ion optics, which are driven with a combination of alternating and direct voltages. By this means the collision cell can be configured so as to transmit ions with minimal losses, even  
15        when the cell is operated at a pressure that is high enough to guarantee many collisions between the ions and the gas molecules.

By careful control of the conditions in the collision cell, it is possible to transmit the wanted ions  
20        efficiently. This is possible because in general the wanted ions, those that form part of the mass spectrum to be analyzed, are monatomic and carry a single positive charge; that is, they have "lost" an electron. If such an ion collides with a neutral gas atom or molecule, the ion  
25        will retain its positive charge unless the first ionisation potential of the gas is low enough for an electron to transfer to the ion and neutralise it. Consequently, gases with high ionisation potentials are ideal target gases.

Conversely, it is possible to remove unwanted artefact  
30        ions whilst continuing to transmit the wanted ions efficiently. This is because the artefact ions are molecular ions, and are much less stable than the atomic ions. In a collision with a neutral gas atom or molecule, a molecular ion may dissociate, forming a new ion of lower  
35        mass and one or more neutral fragments. In addition, the collision cross section for collisions involving a molecular ion tends to be greater than for an atomic ion.

This was demonstrated by Douglas (Canadian Journal Spectroscopy, 1989 vol 34(2) pp 38-49).

However, when the collision cell is operated at a pressure that is sufficiently high to promote removal of the artefact ions that originate in the plasma, other artefact ions may form. The chemical nature of these ions is not always known with certainty, but, for example, hydrocarbons that are present in the residual gas composition may be ionised by charge exchange. Various species of metal oxide and/or hydroxide ions such as  $\text{LaO}^+$  and  $\text{LaOH}^+$  have been observed, apparently formed in ion-molecule reactions in the cell. Water adduct ions such as  $\text{LaO} \cdot \text{H}_2\text{O}^+$  have also been observed. The artefact ions that are removed in the collision cell can also be generated there, for example by reactions such as:



so that the extent to which such ions are removed from the beam will depend on the equilibrium of two or more reaction pathways.

Even when no collision gas is being admitted to the cell, the local pressure in the cell can be quite high, due to the directed gas load from the plasma itself. Calculations based on the work of Douglas indicate that a pressure of  $1 \times 10^{-3}$  mbar or even higher is quite possible. The gas load from the plasma is composed primarily of the plasma support gas, and so is generally neutral argon. However, it will contain other species, typically hydrogen and oxygen if the sample is dissolved in water, and probably organics, for example from rotary pump oil from the expansion chamber; which is the coarse vacuum stage commonly employed in ICPMS as the first stage of pressure reduction.

If the cell contains a significant partial pressure of argon, this will upset the operation of the instrument in two ways. Firstly, the ion beam will be attenuated by collisions between the ions in the beam and argon neutrals. Secondly, the presence of a large concentration of argon

neutrals will favour the production of argon-containing molecular ions in reaction with ions in the beam. Similar considerations apply to other contaminants, in particular the organics, which have the potential to generate a rich spectrum of mass peaks.

It is an objective of this invention to provide a means whereby the formation, or re-formation, or unwanted artefact ions in a collision cell or other ion transport system may be minimised.

According to the present invention, a mass spectrometer comprises means for generating ions from a sample introduced into a plasma, a sampling aperture for transmitting some of the ions into an evacuated expansion chamber along a first axis to form an ion beam, a second aperture for transmitting some of the ion beam into a first evacuated chamber maintained at high vacuum, an ion optical device located in the first evacuated chamber for containing the ion beam, a third aperture for transmitting the ion beam into a collision cell pressurized with a target gas and disposed in a second evacuated chamber maintained at a lower pressure than the first evacuated chamber, mass-to-charge ratio analysing means located in a third evacuated chamber maintained at lower pressure than the second evacuated chamber and disposed along a second axis for mass analysing the ion beam to produce a mass spectrum of the ion beam.

Preferably, the first evacuated chamber is maintained at a pressure of approximately  $10^{-2}$  to  $10^{-4}$  mbar, more preferably approximately  $1-2 \times 10^{-3}$  mbar.

The provision of the first evacuated chamber between the expansion chamber and the collision cell reduces the gas load on the collision cell, by minimising the residual pressure within the collision cell that is attributable to the gas load from the plasma source, and ensuring that the neutral gas composition within the collision cell is essentially that of the collision gas itself. The ion optical device located in the first evacuated chamber



enables sufficient transmission of ions through the first evacuated chamber.

Preferably, the distance between the ion source and the collision cell is 100 to 200mm. This contributes further to reducing the gas load on the collision cell and ensures that the neutral gas composition within the collision cell is essentially that of the collision gas alone.

Preferably, the mass-to-charge ratio analysing means includes a main mass filter which preferably is an RF quadrupole, although a magnetic sector or a time-of-flight analyser may alternatively be employed.

The ion optical device may be a static lens stack, an electrostatic ion guide, or an electrodynamic ion guide such as an RF multipole. Preferably, the ion optical device is a mass selective device. It is advantageous to employ a quadrupole, since this can be driven so as to transmit only ions of a specific mass to charge ratio ( $m/e$ ) or a range of  $m/e$ . It thus functions as an auxiliary mass filter. A magnetic sector could be employed in a similar fashion. The auxiliary mass filter can be advantageously employed to first reduce the contribution of artefact ions to the mass spectrum, since it is set to transmit only ions from the same  $m/e$  as the main mass filter. Any artefact ion that is formed in the collision cell must therefore be a reaction product from an ion of the  $m/e$  that is selected in both the auxiliary mass filter and main mass filter. The artefact ion must have a different  $m/e$  from that selected, and so will not be transmitted by the main mass filter. Hence the mass spectrum is essentially free from artefact ions. For example, if the auxiliary mass filter is tuned so as to transmit essentially the ions of  $m/e$  56, then the ions that enter the collision cell will be  $^{56}\text{Fe}^+$  and  $^{40}\text{Ar}^{16}\text{O}^+$  (an unwanted molecular ion that is formed in the plasma source). In the collision cell,  $^{40}\text{Ar}^{16}\text{O}^+$  will be lost, while  $^{56}\text{Fe}^+$  is transmitted efficiently. Although molecular or adduct ions may be formed, such as  $^{40}\text{Ar}^{16}\text{O}^+$  at

m/e 72 or  $^{56}\text{Fe}.\text{H}_2\text{O}^+$  at m/e 74, these cannot cause mass spectral interference as the main mass filter is set instantaneously to pass only ions of m/e 56. The auxiliary mass filter and the main mass filter scan synchronously, so if the main mass filter is set to transmit m/e 72, no  $^{56}\text{Fe}^{16}\text{O}^+$  can form in the collision cell because the auxiliary mass filter will have removed  $^{56}\text{Fe}^+$  from the beam before it can enter the collision cell. Similar arguments apply to artefact ions formed by the fragmentation of molecular ions.

A further advantage of making the ion optical device a mass selective device, such as a quadrupole, is that the most abundant ions in the plasma beam are rejected by the mass selective device. The ion beam that leaves the device is much less intense, and exhibits little or no tendency to diverge under the influence of space-charge. It is therefore much easier to design the subsequent stages of ion optics to transport the beam efficiently.

Preferably the second axis of the mass to charge ratio analysing means is offset from the first axis. This is effective in reducing the unresolved baseline noise signal that is generally present in ICPMS instruments).

Preferably, the first evacuated chamber is divided into a first region adjacent to the expansion chamber, and a second region adjacent to the collision cell, by a large diameter aperture. The ion optical device is located in the second region, and the first region may contain an extractor lens driven at a negative potential. Preferably the diameter of the aperture is approximately 20mm, and it is preferably sealable. This may be achieved by means of a flat plate on an O-ring seal. This enables the second region to be isolated and maintained at a high pressure while the expansion chamber and the first region are vented to atmospheric pressure. This facilitates access to the components most prone to contamination, so that they can be readily replaced or refurbished.

The invention is described by reference to figure 1, which shows a preferred embodiment.

The inductively-coupled plasma (ICP) ion source 1 is of conventional design, operating at atmospheric pressure. Ions are generated in the plasma and entrained in the general gas flow, part of which passes through a sampling aperture 2. The expansion chamber 3, is located behind the sampling aperture 2 and is evacuated by means of a rotary-vane vacuum pump at 4. The gas flow that passes through the first aperture 2 expands as a super-sonic free jet, the central portion of which passes through the second aperture 5 and the first evacuated chamber 6. Aperture 5 is in the form of a skimmer, for example such as described in US patent 5051584. The first evacuated chamber 6 is maintained at high vacuum by a high-vacuum pump, preferably a turbo-molecular pump, located at 7. The pressure in the first evacuated chamber may be of the order of  $10^{-2}$  to  $10^{-4}$  mbar, depending on the size of pump used, but is typically  $1-2 \times 10^{-3}$  mbar.

The sample beam is believed to pass through the aperture 2 in a substantially neutral state. Under the influence of the extractor lens 8, which is driven at a negative potential, typically -200 to -1000 volts, electrons are diverted rapidly from the beam, and positive ions are accelerated away from the aperture 5 along the axis of the instrument. They are focused by an ion lens 10 through an aperture 11, of relatively large diameter, typically about 20mm. A flat plate 12 slides on an O-ring seal 13 and can be moved so as to completely obscure and seal the aperture 11. The aperture 11 divides the first evacuated chamber 6 into a first region 14 and a second region 15. Chamber 6 must be pumped efficiently, and so region 15 must offer a relatively unrestricted conductance. Preferably it will be at least as wide as the diameter of the high-vacuum pump 7.

When the plate 12 is retracted, aperture 11 provides a large pumping conductance, so that regions 14 and 15 are

at essentially similar pressures, although the pressure in the region 14 closer to the skimmer may be marginally higher. The whole of the first evacuated chamber 7 is maintained at high vacuum by means of the high-vacuum pump at 7.

When the plate 12 is positioned so as to block the aperture 11, the region 15 is still maintained at high vacuum. However, region 14 is then pumped only via aperture 3, and so the pressure in region 15 becomes essentially that of the expansion chamber 5 between apertures 2 and 3. It is then possible to vent the expansion chamber 5 and region 14 to atmospheric pressure whilst maintaining high vacuum in region 15. This facilitates access to the components most prone to contamination, so that they can be readily replaced or refurbished.

The ions that have passed through aperture 11 are directed by an ion lens 16 into an ion optical device 17. Device 17 assists in containing the ion beam, which otherwise would tend to diverge rapidly under the influence of positive ion space-charge, and cause severe loss of sensitivity. Device 17 may be a quadrupole, a higher order multiple, an ion guide or an ion lens. As mentioned above, it is advantageous if the transmission-enhancing device can be made to be mass-selective. Preferably it will be a quadrupole, although in principle another mass selective device, such as a magnetic sector, could also be employed.

Ions transmitted by device 17 are focused by the ion lens 18, and pass through an aperture 19 into the second evacuated chamber 20, maintained at a pressure lower than that of the first evacuated chamber 6 by a high-vacuum pump, preferably a turbo-molecular pump, located at 21. The pressure of this chamber is of the order  $10^{-3}$  to  $10^{-5}$  mbar, typically  $1-2 \times 10^{-4}$  mbar. Aperture 19 has a relatively small diameter, typically 2-3mm, thus establishing a pressure differential between the first evacuated chamber 6 and the second evacuated chamber 20.

This reduces the gas load on chamber 20, and so minimises any residual pressure in the chamber 20 due to the neutral gas load from the plasma. It is advantageous if aperture 19 is mounted on an insulator 22, so that it can be biased negative, causing ions to pass through it with relatively high translational energy. This helps to ensure efficient transport of the ions through the aperture 19 both by lowering the charge density within the beam and by minimising the beam divergence.

The ions are focused by ion lens 23 into a collision cell 24, which is located in the second evacuated chamber 20. Located in collision cell 24 is a multipole ion optical assembly 25. This may be a quadrupole, hexapole or octapole. The collision cell 25 is pressurised with a target gas 26, chosen for its capacity to remove, via a mechanism such as attachment or fragmentation, unwanted molecular ions from the ion beam whilst influencing other ions minimally. Typically the target gas may be helium or hydrogen, although many other gases may prove beneficial for specific analytical requirements, particularly inert gases such as argon.

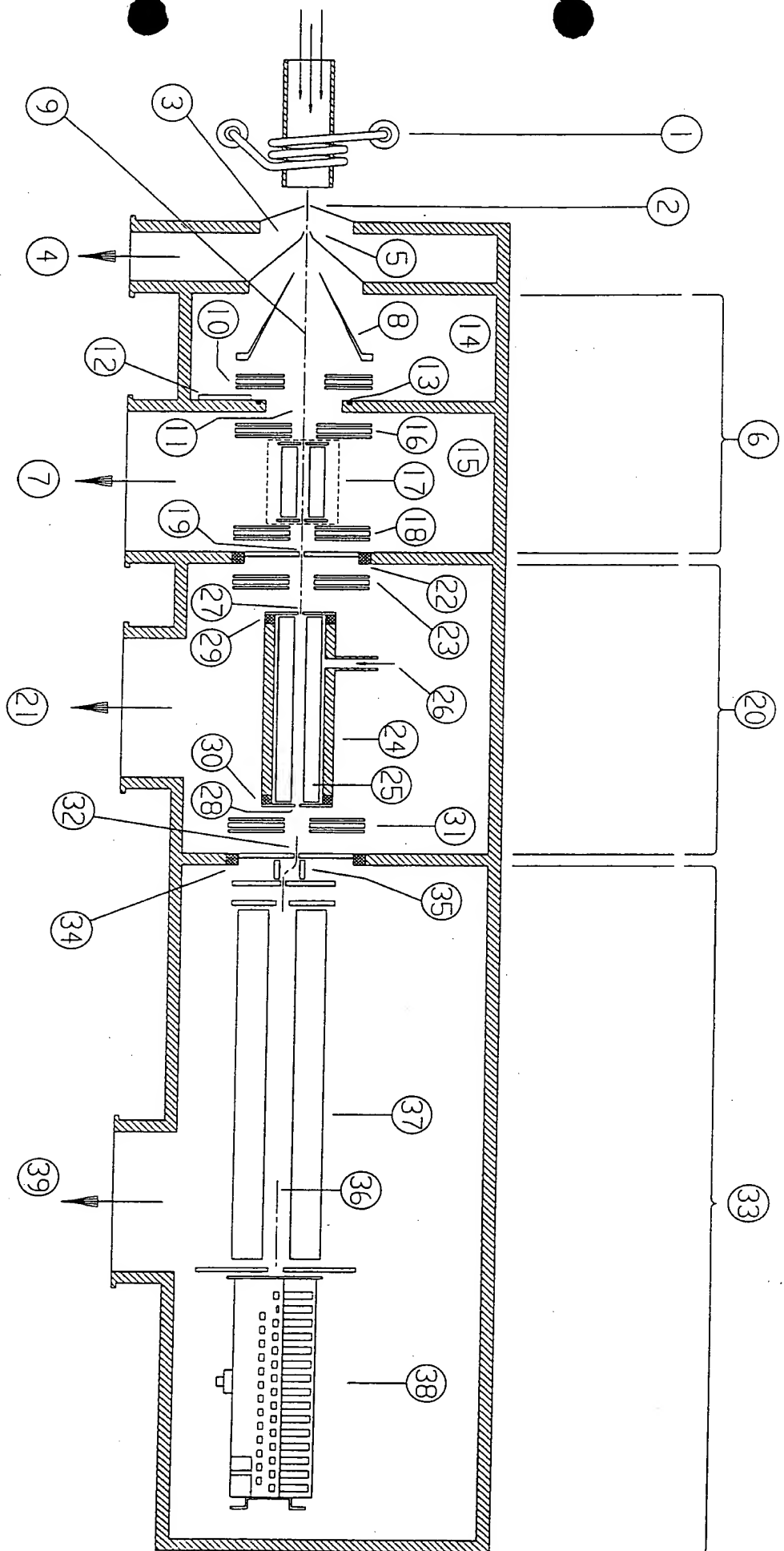
Apertures 27 and 28 limit the gas conductance out of the collision cell, thus allowing it to operate at a relatively high pressure whilst minimising the gas load on chamber 20 and its associated high vacuum pump 21. The transport efficiency of ions through apertures 27 and 28 is improved by biasing the apertures negative. They are mounted on the collision cell by means of insulating gas-tight supports 29 and 30.

Ions that leave the collision cell are accelerated and focused by ion lens 31 through an aperture 32. This aperture establishes a pressure differential between chamber 20 and the third evacuated chamber 33 thus reducing the gas load on chamber 33, and further minimising any residual pressure therein due to the neutral gas load from the plasma. It is advantageous to mount aperture 32 on an insulating support 34. The aperture 32 can be then biased

negative with respect to ground, typically to -100 volts, so that ions pass through it with relatively high translational energy. This helps to ensure efficient transport of the ions through aperture 32 both by lowering the charge density within the beam and by minimising the beam divergence.

The ions pass through aperture 32 at relatively high translational energy, and pass through a double deflector 35 preferably at the same time or higher energy. This deflects the ion beam away from the original instrument axis 9 and along the axis 36 of the quadrupole mass filter 37, which is used to mass analyze the ion beam. The double deflector 35 is advantageously in the form of two small cylindrical electrostatic sectors, cross-coupled and in series. We have found this configuration to be especially effective in reducing to below 1 CPS the unresolved baseline noise signal that is generally present in ICPMS instruments.

Ions of the selected  $m/e$  or range  $m/e$  are transmitted to a detector, which is typically an electron multiplier 38. The first dynode of the electron multiplier 38 is offset from axis 36 of the quadrupole mass filter, which further helps to minimise the unresolved baseline noise signal. Both the mass filter 37 and the detector 38 are housed in the third evacuated chamber 33, which is maintained at a pressure lower than that of the second evacuated chamber 20 by a high-vacuum pump 39. The pressure of this chamber is less than  $10^{-4}$  mbar, typically about  $10^{-6}$  mbar, although certain types of ion detectors can operate at pressures as high as  $2-5 \times 10^{-5}$  mbar.



PCT/GB 99/03076

GILL JENNINGS & EVERY

16/9/99